11.5 FLUOROMETERS

Fluorometers are useful in detecting dyes for Time-of-Travel and dilution studies in streams. Fluorometers are also useful in detecting detergents that are commonly found in domestic wastewater and septic systems, and for detection of septic systems leakage into lakes and streams.

11.5.1 Stream Time-of-Travel

A. GENERAL

Three principal methods are used to determine travel time in streams. These methods are surface floats , measurements of cross sectional velocity, and tracers (dye).

A rough method for preliminary estimates of time-of-water travel con sists of dropping sticks or other buoyant objects from bridges into the stream reach under observation, and noting the time required for them to float an estimated 3.1m (10ft) or another convenient distance. The velocity estimates are too inaccurate for use in interpretation of data or final reporting, but can be useful in preliminary planning of studies and in subsequent more precise measurements of time-of-water-travel.

Stream velocities at gaging stations, measured by the U. S. Geological Survey in developing rating curves, may be applied to the entire reach under observation to estimate time-of-water travel. This is more refined than using floating objects, but can still be inaccurate. Rarely are there more than one or two gaging stations in most stream reaches being studied. Stream channels generally are restricted at gaging stations and velocities are generally higher than average velocities throughout the reach. Cross sectional velocities can also be determined at locations designated for a particular study.

Tracer dyes provide a direct and highly accurate method of determining time-of-travel. This is the preferred method if resources are available.

B. PROCEDURES

Floats -- Surface floats may be followed downstream and timed for known distances to determine time-of-water-travel. This requires the use of considerable judgment, for floats tend to travel into quiet or eddy areas, or to become stuck on tree limbs, the stream bank, or other obstacles. The floats must frequently be retrieved and returned to the stream current. The principal judgment factors are how long the floats should be left in quiet areas before retrieval and where they should be placed in the current.

Surface water velocity is greater than the average for the entire stream, and a correction factor must be applied to the surface velocity. An average velocity of about 85% of the surface velocity is a reasonable rule-of-thumb value.

Cross Section Measurements -- The measurement of cross sectional velocities at frequent longitudinal intervals and the calculation of average velocity in the stream is a time-consuming method of obtaining time-of-water-travel.

The longitudinal intervals at which cross sections shall be measured vary with the characteristics of the stream channel. One cross section per 1.6km (1.0mi) may be adequate for streams with reasonably uniform channels. Cross sections at every 0.16km (0.1mi) may be desirable for streams with irregular channels.

Tracers -- The most accurate method of measuring time-of-travel involves following a tracer. Some conservative industrial waste constituents, salt, or radioisotopes may serve as tracers; however, dye is most common. The most frequently used dye is Rhodamine WT; it can be detected in concentrations as low as 0.01ppb by a fluorometer.

Before injection into the stream, the concentrated dye shall be diluted with the stream water. This shall help insure immediate maximum dispersion. Addition of concentrated dye without dilution may incur incomplete dispersion, particularly in shallow streams. Calibration curves shall be developed for each study with particular emphasis on accounting for natural background fluorescence.

The dye should be distributed across the stream at a upstream point, as nearly instantaneously as possible. The ideal distribution produces a narrow band of tracer in uniform concentration across the stream. The band of tracer mixes with water ahead of and behind it by diffusion, and longitudinal mixing, as it moves downstream to produce an increasingly wider band. The peak concentration remains near, but downstream, the center line of the band and decreases as longitudinal mixing proceeds. Times-of-water-travel to downstream points are the differences between the time the dye was added to the stream and the times the centroid of the dye mass arrives at downstream points. The length of the dye cloud and the peak concentrations produces a measure of instream dispersion.

If Rhodamine WT dye is used as a tracer, peak concentrations from 1.0 to 50.0ppb allow satisfactory definition of the dye concentration curve.

Most methods of calculating the dosage of dye needed at the upstream point involves estimates of one or more stream characteristics, such as flow, velocity, length of reach, volume in the reach, cross sectional area, average depth, and the roughness coefficient, "n", of the Manning's formula. USGS has produced excellent publications regarding time-of-travel techniques, i.e., "Measurement of Time-of-Travel and Dispersion by Dye Tracing" (9) and "Fluorometric Procedures for Dye Tracing" (10).

The stream shall be sampled frequently as the dye arrives at the downstream point to define the tracer concentration versus time curve with special emphasis on the peak. The frequency may be varied from once every minute to once every 10 to 15 minutes, depending on how wide the band of dye has become at the sampling point. The dye may be missed completely by overestimating the time required for it to travel downstream. Much time may be wasted, on the other hand, waiting for it to arrive if the time-of-travel is underestimated. All information that shall contribute to the best possible preliminary estimate of the required time shall be used.

Two primary methods are used for sampling and analyzing the dye in a stream. A submersible pump can be used to pump dye continuously through a fluorometer, or the stream samples can be grabbed either by hand or by automatic sampler at specified frequencies then placed into the fluorometer individually. With the "flow-through" version, a strip chart recorder connected to the fluorometer can be used to plot the tracer concentration versus time. Readings directly from the fluorometer scale or conversion to dye concentration can be manually plotted against time when using the grab sampling technique.

A version of the grab sampling technique would be using an automatic water sampler that discharges into separate bottles. The sampler is preset to collect samples at certain intervals; at the end of the sample collection time, the discrete samples would be analyzed and the concentration determined for each sample. The concentrations are then plotted against time.

For proper determination of travel time, samples shall continue to be analyzed until the stream background concentration following the peak is measured. With a time versus concentration plot which coincides with the background level to peak to background level, the centroid or the actual travel time can be determined.

The Drinking Water Program shall be contacted before conducting tracer studies in freshwater systems to insure that tracer concentrations do not impart color to downstream public or private water supplies.

C. EQUIPMENT AVAILABLE

The following DEQ equipment is available for time-of-travel studies:

- tracer standards
- pumps
- recorders
- flow meters
- floats

11.5.2 Dilution Studies

A. PROCEDURES

Much of the information discussed in the stream time-to-travel studies applies to dilution studies. USGS publication "Measurement of Discharge by Dye-Dilution Methods" (11) provides references for the techniques .

Dilution studies using tracer dyes evolve from "mass conservation" prin ciples. That is, a known mass of a tracer is introduced at an upstream point, and after mixing with the water to be traced, this mass should be accountable at downstream locations. Rhodamine WT provides an adequate tracer for such investigations. This dye is slightly photoreactive and reaction rates are available in the literature (generally, K rate is 0.034/day). The technique of choice is the use of fluorometers with tracer dyes due to the high degree of accuracy and detection ability of fluorometers plus the solubility properties of tracer dyes.

In dilution studies, the tracer dye is precisely metered into the waters to be traced and then monitored after mixing by a fluorometer at downstream stations. This series of events requires highly controlled metering rates and very accurate fluorometric analyses.

B. EQUIPMENT AVAILABLE

The following DEQ field equipment is available for dilution studies:

- fluorometer
- metering pump
- tracer standards
- pumps

C. SPECIFIC EQUIPMENT QUALITY CONTROL PROCEDURES

Refer to the quality control section in the previous section. The metering pump are calibrated before and during use; the field calibration data are recorded in the field records.

Investigations of industrial and municipal facilities for NPDES permit compliance require measurements of discharge rates. Often encountered during these investigations are flow measuring devices such as orifices and magnetic meters that are inaccessible for flow measurements by standard equations relating to hydraulic head and structure size. The following provides a direct technique for flow measurement through orifices and magnetic meters using dye tracers.

Discharge rate through any structure can be defined by the following mass balance equation:

MASS BALANCE EQUATION

$$Q_2 = \frac{(C_1)\ (q_1) - (C_2)\ (q_1)}{C_2}$$

Where:

Q_2 = pipe flow rate
C_1 = tracer injection concentration
C^2 @ (Q_2+q_1)
q_1 = tracer injection rate
C_2 = tracer concentration after mixing
q_1 @ C_1
$(C_1)(q_1) = (C_2)(Q_2 + q_1)$

Assuming a constant discharge rate and complete mixing of a tracer material in the waste stream, the task is (1) to inject a tracer material into the waste stream at a constant rate and constant concentration, and (2) to measure the concentration of the tracer after mixing with the waste stream.

11.5.3 Groundwater Time-of-Travel and Hydrologic Connections

A. EQUIPMENT

1. 250ml sample bottles (polyethylene plastic or glass)

2. Rhodamine dye

3. Ice chest

4. Injection equipment as needed such as funnel and hose

B. PREPARATION

1. Selection of the dye injection site is dependent on the problem to be examined. Injection sites may include septic tank, drainfield, well, etc. Volume of dye to be injected depends on the estimated soil characteristics, flow volume, distance, and time-of-travel. Rhodamine WT concentration shall not exceed 100ppb in a groundwater study nor 0.1ppb in a drinking water supply. The Turner 450 Fluorometer can detect Rhodamine dye at less than 1.0ug/L concentration under ideal conditions.

2. Any dye injected into a well shall be nontoxic and placed at or near the screen. Dye injection shall be accomplished using a sufficient volume of water to insure movement into the flow system to be examined. For example, a well shall be surged with 3 well volumes following the introduction of dye after determining the well to be dyed is under the influence of the pumped well. A septic tank shall be surged with at least 1 volume following dye introduction with consideration given to the infiltration limitations of the drainfield, if any.

C. COLLECTION

1. Background samples shall be collected before any introduction of a dye into the flow system. Well background samples shall be obtained following pumping of the well to insure stabilized temperature and pH. Background stream or pond water sample sites are

dependent on the problem to be examined. Background samples are critical to fluorescence testing with high "blank" fluorescence being the most limiting factor relating to sensitivity of the test.

2. Following dye injection, samples shall be obtained from the selected sites over a period of time. The

start and end time are dependent on factors described in 2.a of the Operator's Reference Manual for Digital Fluorometer Model 450 with sampling periods ranging between 1-30 days.

3. Sample bottles shall be identified with specific site ID number, name of sampler, date, and time of collection.

D. PRESERVATION

1. Samples must be cooled to 4 °C and maintained in darkness until analyzed.

E. PRECAUTIONS

1. Be sure to triple rinse the sample bottle with the source water before the collection of the sample.

2. Check sample bottles to make sure they are properly identified with the required information.

F. QUALITY CONTROL

1. Background and target samples must be from the same sample locations.

2. Timing of the sample collection shall coincide to minimize diurnal influences. For example, all samples shall be collected at same time each day and collection time of the background sample.

3. Samples shall be held no more than 2 weeks before analysis.

G. SPECIAL INSTRUCTIONS

Fluorescence can be useful in determining hydraulic connections and flow rates based on introduced dyes. Specific dyes require specific filters on the fluorometer. Be sure to match your dye with available filters.

Sewage impacts can be documented using the fluorescent properties of detergent whiteners and specific filters on the fluorometer. Be sure the waste stream contains detergents with whiteners before sampling.

The Turner 450 Fluorometer can be used in the field at a site with 120V power.

H. REFERENCES

Operator's Reference Manual, Model 450 Digital Fluorometer. Sequoia-Turner Corporation, 1987.

Case Studies in WHP Delineation and Monitoring. U.S. EPA-

600/R-931, pg. 4-18 through pg. 4-60, 1993.

11.5.4 Fluorometric Determination of Dye Tracer

A. SCOPE AND APPLICATION

This method covers the determination of fluorescence as it relates to com mercially available tracer dyes. Rhodamine dyes are fluorescent at a wavelength of 590 millimicrons, making them detectable without major interferences in all natural waters.

B. SUMMARY OF METHOD

Fluorescent dyes emit light upon irradiation from an external source. The emitted light is proportional to the tracer concentration within the sample.

C. SAMPLE HANDLING

- Since tracers are photoreactive, care must be taken to protect samples from light sources.
- All samples shall be stored in glass containers.

D. INTERFERENCES

- Temperature shifts the fluorescent properties of the tracers; thus all samples shall be analyzed at the same temperature as the calibration standards.
- Natural conditions such as the presence of chlorophyll or tannins and lignins in the waters to be traced can impart background fluorescence. Cali bration standards shall be made from these ambient waters to account for any potential background.
- Sample tu rbidity may interfere. In highly turbid waters, accuracy may be enhanced by filtration before analysis.

E. APPARATUS

- Turner Fluorometer Model 10-005
- Calibration glassware

F. STANDARDS

1. Flow-Through Configuration

Working stocks (use a water sample from the study areas as dilution water).

a) Dilute 1ml dye to 1 liter dilution water: solution "A" = lppt.
b) Dilute 10ml of solution "A" to 1 liter solution "B" = 10ppm.
c) Dilute 100ml of solution "A" to 1 liter solution "C"= 100ppm.

2. Cuvette or Pour-Through Configuration

Working stocks (use a water sample from the study area as dilution water).

a) Dilute 10ml dye to 1 liter: solution "A" = 10ppt.
b) Dilute 10ml "A" to 1 liter: solution "B" = 100ppm.
c) Dilute 1ml "A" to 1 liter: solution "C" = 10ppm.
d) Dilute 10ml to 1 liter: solution "D" = 1ppm.

From these stocks

a) Each ml "B" to 1 liter adds 100ppb
b) Each ml "C" to 1 liter adds 10ppb
c) Each ml "D" to 1 liter adds 1ppb

G. PROCEDURE

1. Turner Fluorometer Model 10-005

a) Allow fluorometer to warm up for 10 minutes.
b) Using background water, adjust for background fluorescence by setting instrument on the most sensitive scale (x31.6 and x100 sensitivity) to read 0.0.
c) Machine circuitry is designed such that one calibration standard, i.e., 100ppb, produces linear responses throughout a range 0.05 to 300.00ppb.

d) Above 300ppb, emissions from the irradiated dye sample interfere with one another producing a nonlinear condition. Thus, when working above 300 ppb, calibration curves are required.
e) Though a single 100ppb standard produces a linear response in the range 0.1 to 300.0ppb, a second standard, i.e., 10ppb, shall be used as a check.
f) Depending upon sensitivity needs, a 100ppb standard can be used to provide a wide range of tracer concentrations. A typical applica tion by the DEQ involves setting a 100ppb standard to equal 10 on the mini mum sensitivity scale (xMS and x100). With this setting, tracer concentrations in the range 0.05 to 300.00ppb can easily be

determined.

H. PRECISION AND ACCURACY

Precision and accuracy for this method have not been established.

I. REFERENCE

Wilson, James F., Jr., Fluorometric Procedures for Dye Tracing : USGS Techniques for Water-Resources Investigations, Book 3, Chapter A12 (1968).

Operating and Service Manual, Model 10 Series Fluorometers, Turner Designs, October 1981.